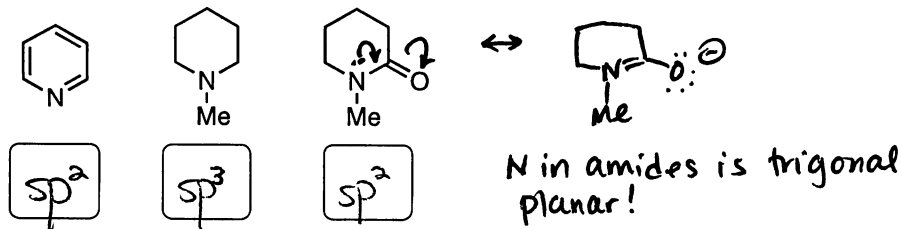


Name: Answer Key

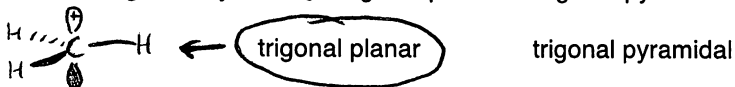
CHEM 633: Advanced Organic Chem: Physical
Problem Set 1: Review & Molecular Orbital Theory

Answers must be in the boxes provided to receive full credit. You may work in groups, but please turn in your own work.

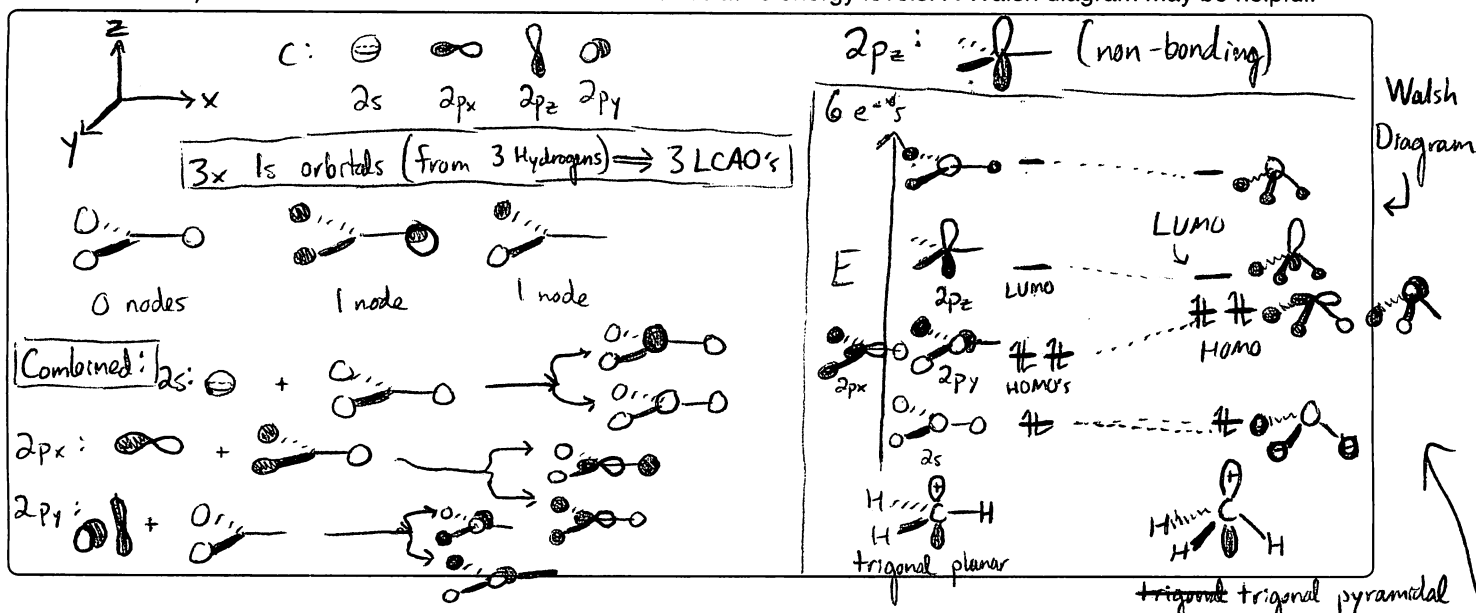
1. Please label the hybridization of the nitrogen atoms in the molecules below.



2. (a) What is the molecular geometry of CH_3^+ : trigonal planar or trigonal pyramidal? (Circle your answer.)



(b) Draw both molecular orbital diagrams to explain your answer to part (a). You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels. A Walsh diagram may be helpful.



(c) Now consider CH_3^- . Rationalize why it is trigonal pyramidal by comparing the appropriate molecular orbital diagrams.

2b) See the Walsh Diagram in 2b for both conformations.

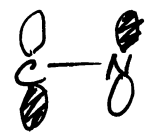
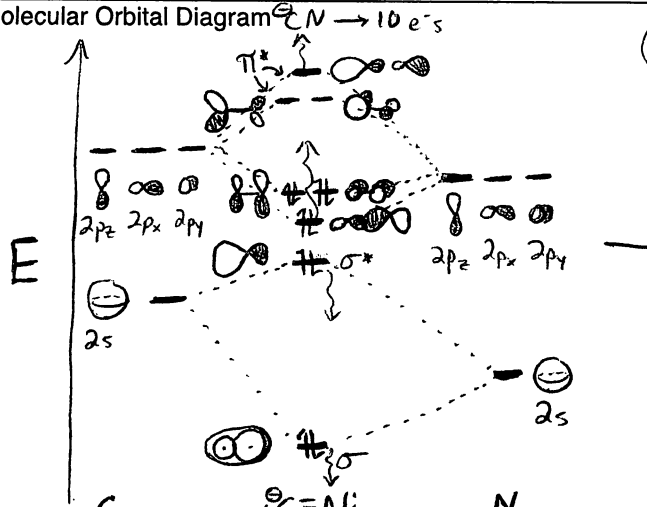
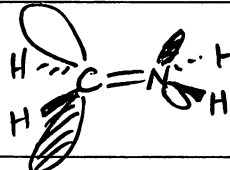
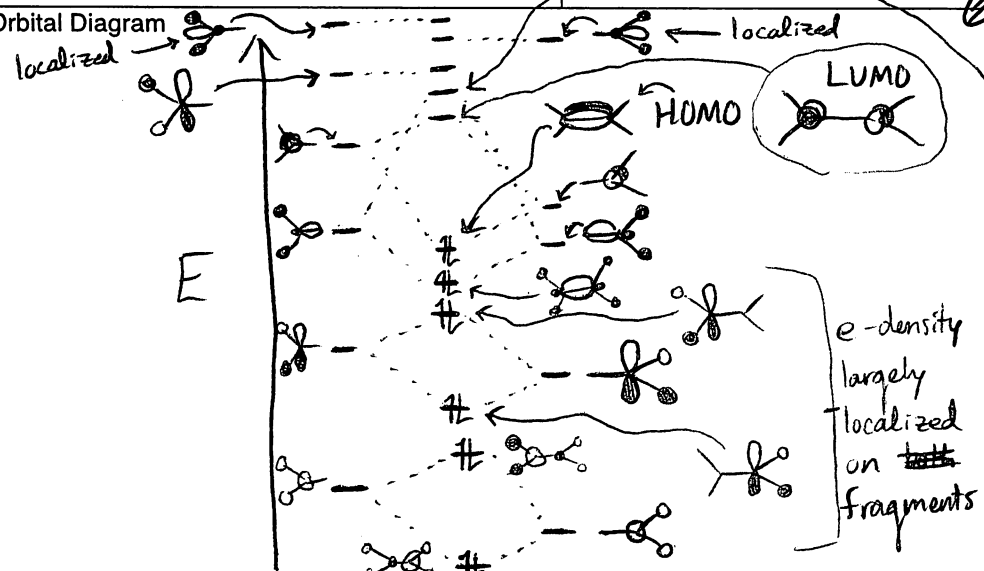
- LUMO is lower in trig. pyramidal geometry due to orbital interaction between $2p_z$ on C and $1s$ on all H's. However, only occupied orbitals matter for relative energy.
- HOMO is higher in trig. pyramidal geometry due to reduced orbital interactions.

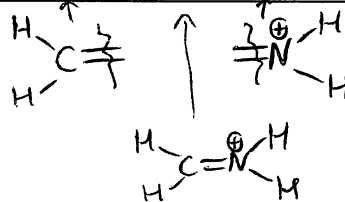
c) For CH_3^- , the $2p_z$ orbital (see Walsh diagram above) becomes the HOMO; since molecular energy/stability is inferred by the HOMO, CH_3^- is more stable in trigonal pyramidal geometry.

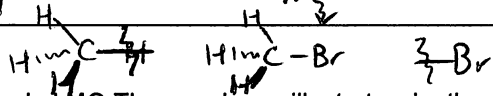
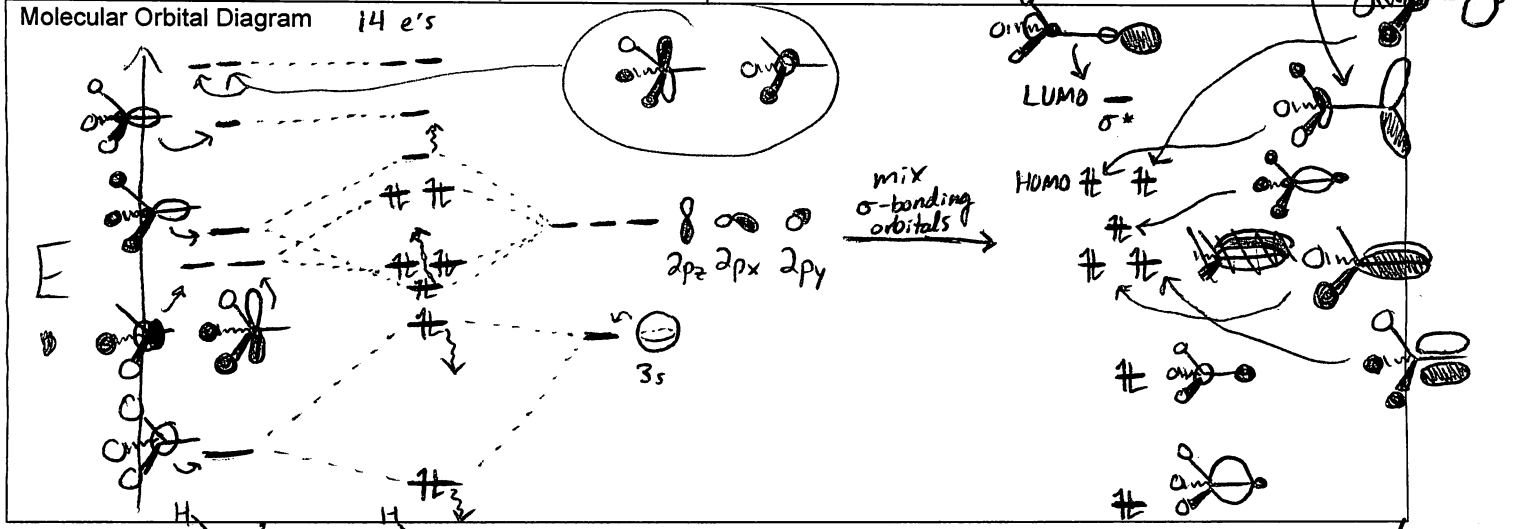
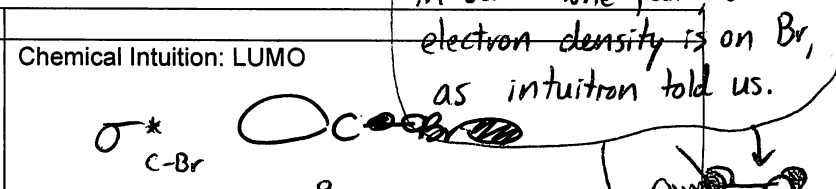
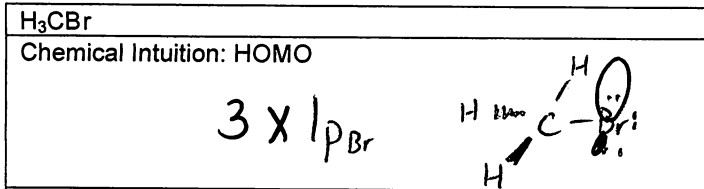
3. (a) Using your "chemical intuition," please name and draw the HOMO and LUMO for the following molecules. Please put your answer in the table below.

- i) CN^- ii) $\text{H}_2\text{C}=\text{NH}_2^+$ iii) H_3CBr

(b) Now, in the table below, construct molecular orbital diagrams for each of the molecules. Clearly label the HOMO and LUMO in each MO diagram. You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels.

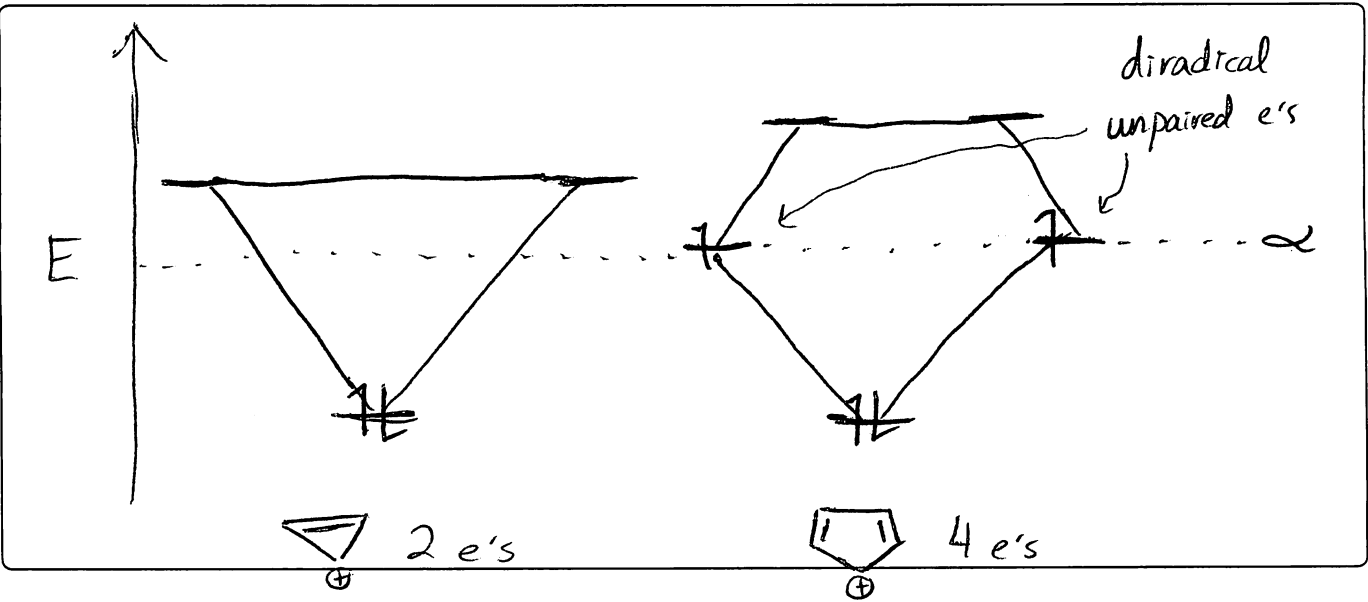
<p>CN⁻</p> <p>Chemical Intuition: HOMO</p> <p>$\text{:C}\equiv\text{N:}$ HOMO = $1p_C$</p> <p>$\text{:C}\equiv\text{N}$</p>		<p>Chemical Intuition: LUMO</p> <p>$\pi^*_{\text{C}\equiv\text{N}}$</p> 	
<p>Molecular Orbital Diagram $\text{C}\equiv\text{N} \rightarrow 10 e^-$</p>  <p>C N</p>		<p>$\text{LUMO} = \pi^*$ ✓ Matches intuition</p> <p>σ^*</p> <p>π^*</p> <p>HOMO \uparrow</p> <p>although e's are delocalized, looks a lot like C $1p$ (lobe is bigger on C than N)</p> <p>$\text{:C}\equiv\text{N:}$</p>	
<p>H₂C=NH₂⁺</p> <p>Chemical Intuition: HOMO</p> <p>$\text{H}_2\text{C}=\text{NH}_2^+$</p> <p>$\pi$</p>		<p>Chemical Intuition: LUMO</p> <p>π^*</p> 	
<p>Molecular Orbital Diagram</p>  <p>C N</p> <p>localized</p> <p>localized</p> <p>HOMO</p> <p>LUMO</p> <p>σ^*</p> <p>e-density largely localized on fragments</p>		<p>localized</p> <p>localized</p> <p>HOMO</p> <p>LUMO</p> <p>σ^*</p> <p>e-density largely localized on fragments</p>	



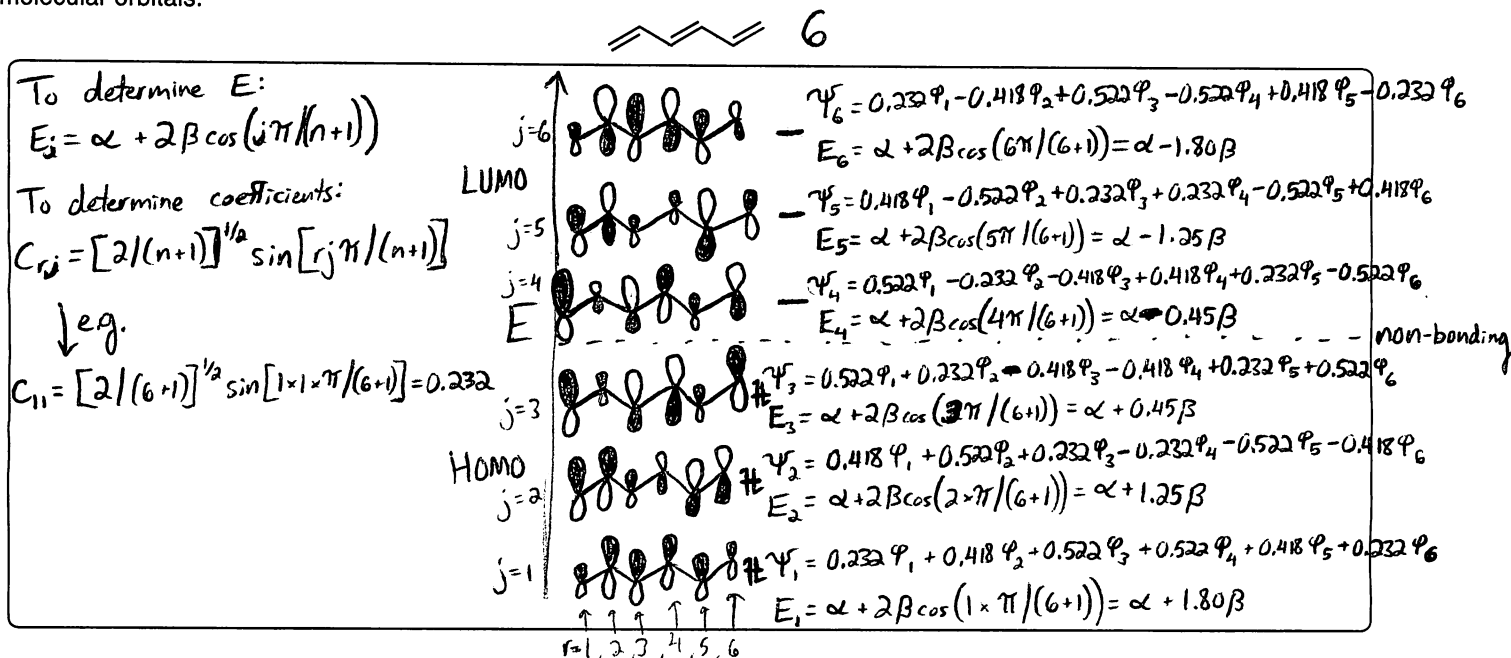


cyclopentadienyl? ← oops! sorry!

4. Using Huckel MO Theory, please illustrate why the cyclopropenyl cation is stable, yet ~~cyclopentadienyl~~ cation is unstable.

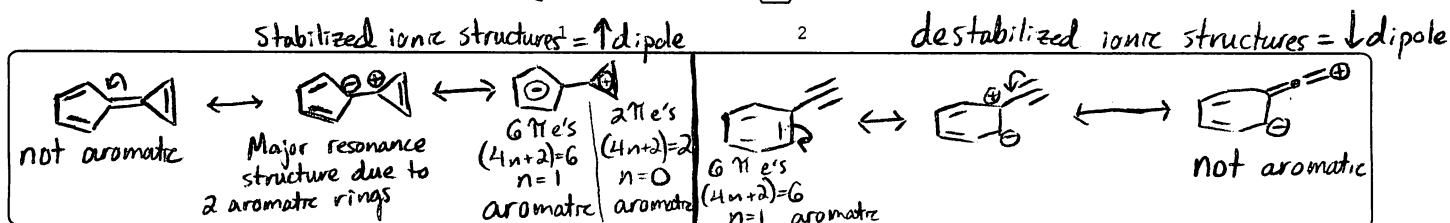


5. Construct a Hückel MO diagram for hexatriene. Label the frontier molecular orbitals. Draw the molecular orbitals. Determine the energy of each MO in terms of α and β . Determine the coefficients of the atomic orbitals in the frontier molecular orbitals.

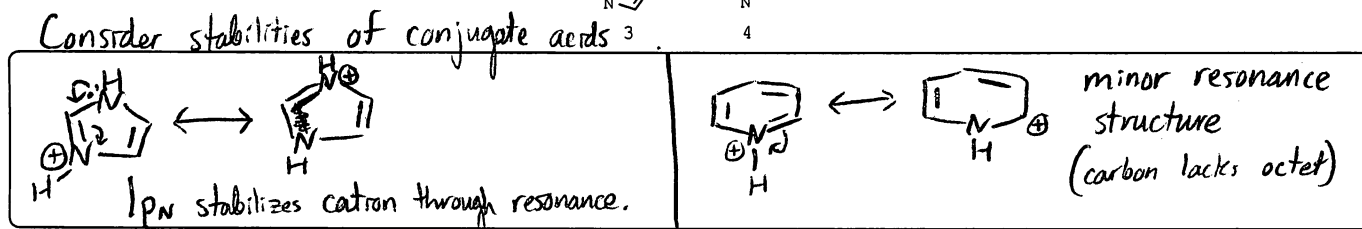
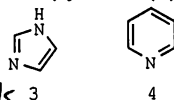


6. (Grossman, Ch 1, #1d,f,g) Explain each of the following observations.

(a) Compound 1 has a much larger dipole moment than its isomer 2.



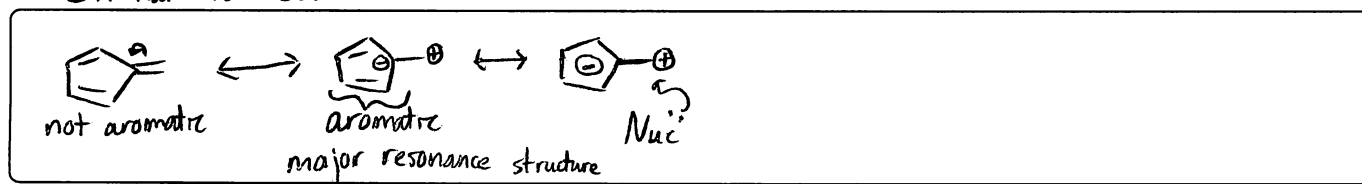
(b) Imidazole (3) is considerably more basic than pyridine (4).



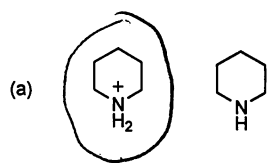
(c) Fulvene (5) is electrophilic at the exocyclic C atom.

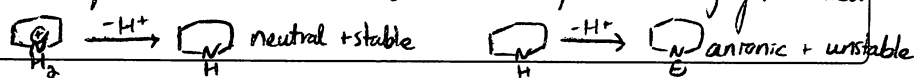


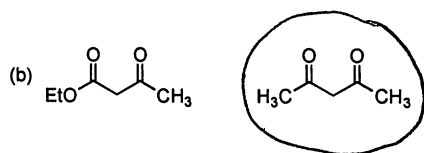
Similar to 6a:

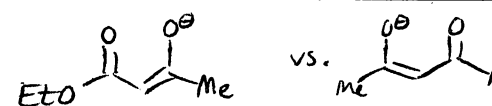
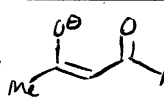


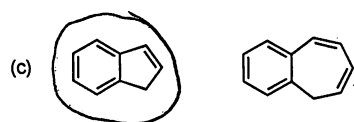
7. (Grossman, Ch 1, #2b,c,d,g,i,j) Please circle which of each pair of compounds is likely to be more acidic and explain why.





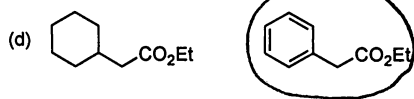
- Piperidinium ~~ion~~ is the conjugate acid of piperidine.
 - Thus, compare the stabilities of their respective conjugate bases:


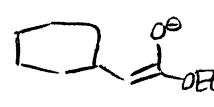
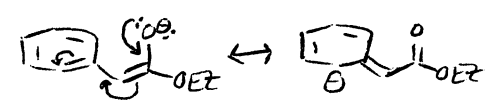


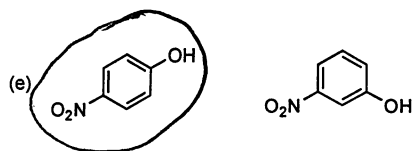
 vs. 
 Ester is less electrophilic than ketone. Also, ester is electron-donating, which destabilizes the anion.


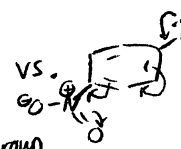


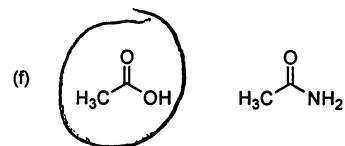
 vs. 
 $(4n+2) = 10$ $n=2$ aromatic vs. $4n = 12$ $n=3$ anti-aromatic

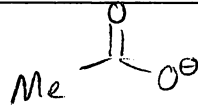
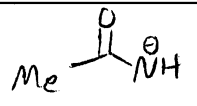


 vs. 
 stabilized by resonance

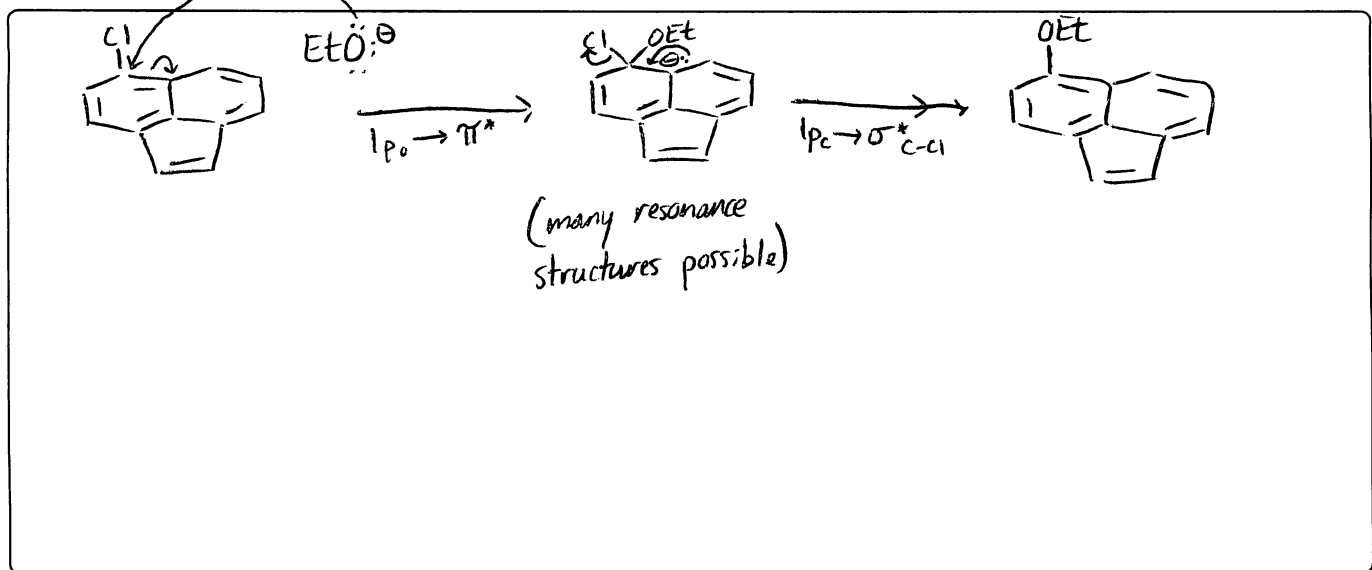
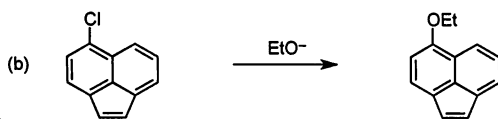
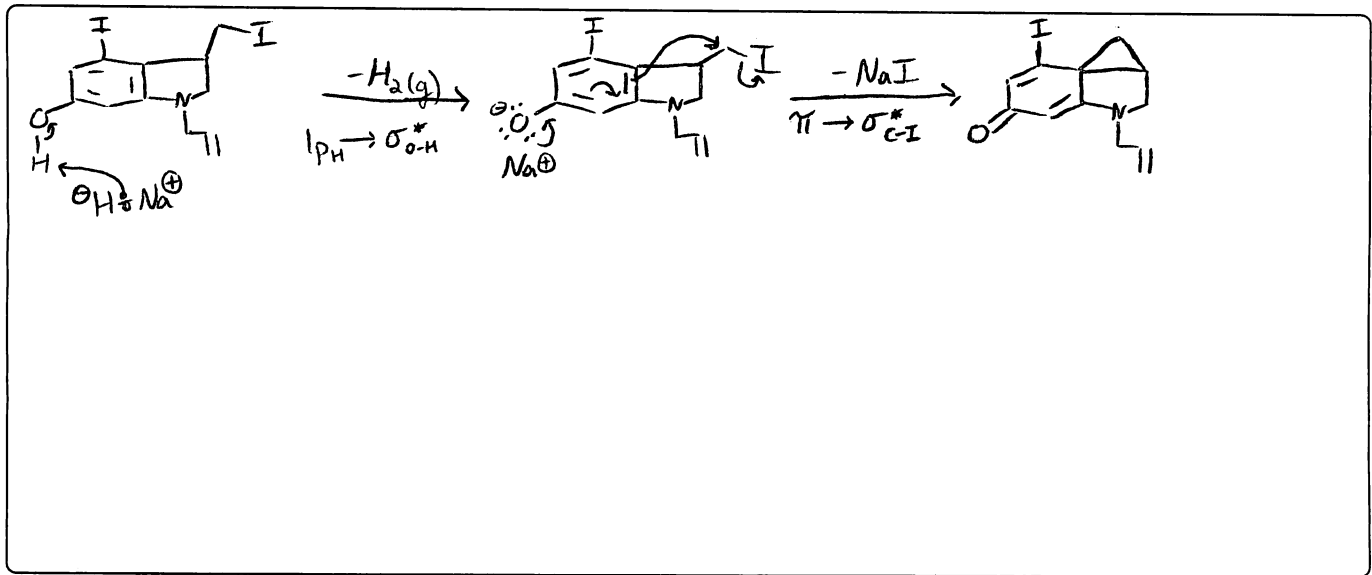
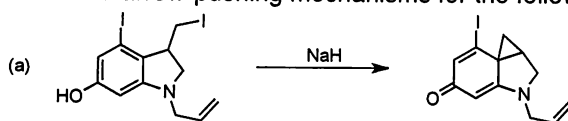


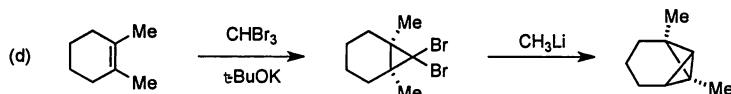
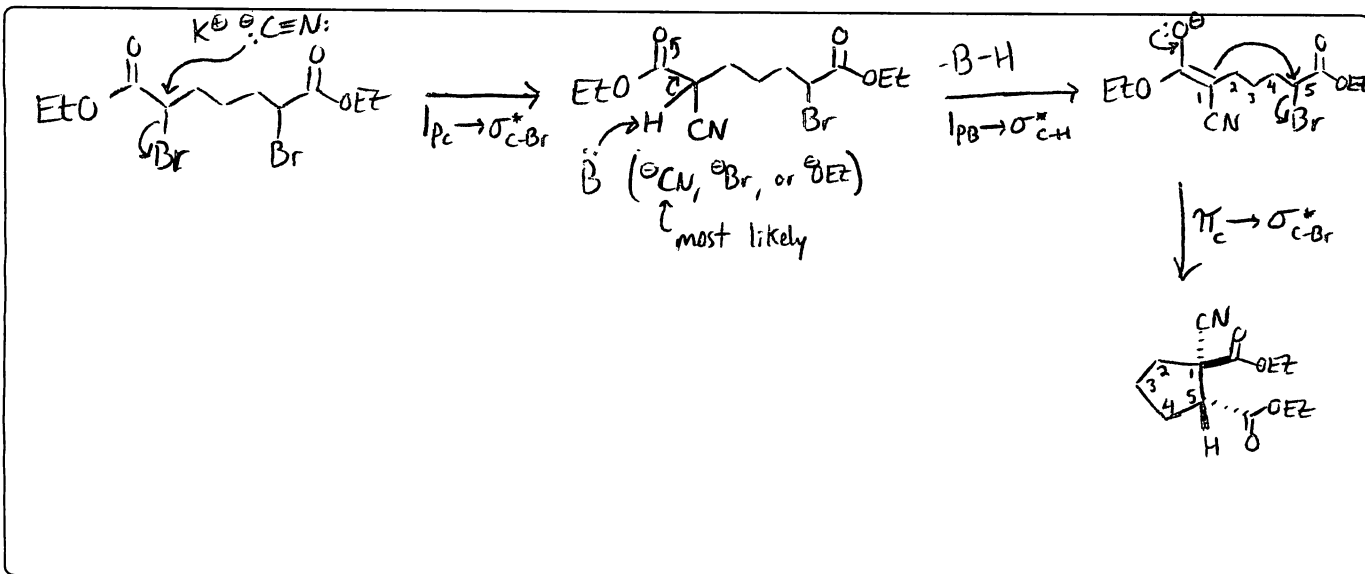
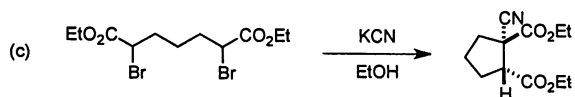
 vs. 
 Can't resonate into NO_2 group vs. stabilized by resonance



 vs. 
 Oxygen is more electronegative than nitrogen

8. (Grossman, Ch 2) Draw reasonable arrow-pushing mechanisms for the following reactions.





Carbene has a lp and an empty p-orbital (acts as both a nucleophile and electrophile)

